THE EFFECTS OF CORE SHELL IMPACT MODIFIER ON PROPERTIES AND CRYSTALLIZATION BEHAVIOUR OF POLY(LACTIC) ACID

by

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TABLE OF CONTENTS

CHAPTER THREE: MATERIALS AND METHODOLOGY

CHAPTER FOUR: RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ATR	Attenuated total reflection
CIE	Commission Internationale de l'Eclairage
CSIM	Core shell impact modifier
CSPN	Core shell acrylic nanoparticles
DGEBA	Diglycidyl ether of bisphenol-A
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetric analysis
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
HDPE	High density polyethylene
HRTEM	High resolution transmission electron microscope
MDS	Material data sheet
MFI	Melt flow index
MMT	Montmorillonite
OMMT	Organoclay-montmorillonite
PBA	Polybutyl acrylate
PBT	Polybutyl terepthalate
PC	Polycarbonate
PE	Polyethylene
PHA	Polyhydroxyalkanoate
PLA	Polylactic acid
PMMA	Polymethyl methacrylate
POM	Polarized optical microscopy
PP	Polypropylene
PS	Polystyrene
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
XHR- FESEM	Extreme High Resolution Field Emission Scanning Electron Microscopy

LIST OF SYMBOLS

M_w	molcecular weight
°C	degree celcius
K	Kelvin
T_m	melting temperature
T_g	glass transition temperature
wt%	weight percentage
T_{cc}	cold crystallization temperature
ΔH_{cc}	enthalpy of cold crystallization
ΔH_m	enthalpy of fusion
X_c	degree of crystallinity
Φ_{PLA}	weight fraction of PLA
T_c	crystallization temperature
L^*	lightness
a^*	red/green coordinate
b^*	yellow/blue coordinate
ΔE^*	total color difference
T_{onset}	onset temperature
$T_{3\%}$	temperature 3% weight loss
$T_{5\%}$	temperature 5% weight loss
T_P	DTG peak temperature
R_{550}	percentage char/residue at temperature 550 °C
X_t	relative degree of crystallinity
N	the Avrami exponent
K	the crystallization rate constant
R^2	the coefficient of determination for the Avrami fit
$t_{½}$	the half-time of crystallization
$\boldsymbol{\tau}_{½}$	crystallization rate

KESAN-KESAN PENGUBAHSUAI HENTAMAN KELOMPANG TERAS TERHADAP SIFAT-SIFAT DAN KELAKUAN PENGHABLURAN POLI(LAKTIK) ASID

ABSTRAK

Polilaktik asid (PLA) telah dicampur leburan dengan kandungan yang berlainan (0 hingga 30% berat) pengubahsuai hentaman kelompang teras (CSIM) yang boleh didapati secara komersil. PLA tulen dan PLA/CSIM campuran telah disediakan melalui pengadun dalaman dan pemampat acuan yang dibentuk menjadi spesimen. Sifat-sifat termal, mekanikal dan morfologi campuran telah dikaji. CSIM tulen menunjukkan bahagian kelompang, antara-fasa dan teras apabila diperhatikan di bawah mikroskopi penghantaran elektron (TEM). Setiap bahagian di dalam CSIM tulen menunjukkan suhu peralihan kaca yang berbeza. Spektrofotometri inframerah transformasi Fourier (FTIR) mengesahkan bahawa kelompang dan teras CSIM tulen masing-masing terdiri daripada polimetil metakrilat (PMMA) dan polibutil akrilat (PBA). Peningkatan dalam kandungan CSIM menurunkan keupayaan PLA untuk menghablur/penghabluransemula, dan suhu penghabluran sejuk beralih kepada suhu yang lebih tinggi. Matrik PLA menunjukkan keserasian yang baik dengan kelompang PMMA pada CSIM. Hal ini telah disahkan oleh ujian dinamik mekanikal analisis (DMA). Dalam ujian gravimetri terma (TGA), kedua-dua PLA dan CSIM tulen menunjukkan penguraian langkah tunggal. Setelah penambahan CSIM, lengkungan tegasan – terikan menunjukkan bahawa kerapuhan PLA tulen meningkat tanpa penambahbaikan dalam kemuluran. Kekuatan tensil, kekuatan modulus, dan pemanjangan takat putus PLA menurun; namun begitu, kekuatan hentaman bertakuk dan tanpa takuk meningkat apabila kandungan CSIM meningkat. Mikrograf

mikroskopi pengimbasan elektron (SEM) menunjukkan dengan penambahan kandungan CSIM daripada 5 hingga 30% berat permukaan patah menjadi lebih kasar berbanding PLA tulen. Lompang-lompang dapat diperhatikan berkemungkinan disebabkan oleh tarik keluar CSIM semasa patah. Kejelasan PLA diuji menggunakan kromameter. Penambahan CSIM tidak menjejaskan kejelasan PLA kecuali pada kandungan 30% berat daripada CSIM. Kinetik penghabluran isoterma PLA tulen dan PLA/CSIM campuran dikaji menggunakan kalorimetri pengimbasan perbezaan (DSC) dan data yang diperolehi dianalisa menggunakan persamaan Avrami. Keputusan menunjukkan bahawa kadar penghabluran dikawal oleh suhu penghabluran dan penambahan kandungan CSIM. Kadar penghabluran maksimum, $\tau_{½}$ dapat dilihat apabila PLA diadun dengan 1% berat CSIM dan penghabluran secara isoterma pada 105 °C. Trend hasil untuk darjah penghabluran (X_c) hampir bersamaan dengan kadar penghabluran ($\tau_{½}$) berbanding suhu penghabluran (T_c). Peningkatan pada $T_c \geq 110$ ° C yang lebih tinggi telah menjadikan pergerakan segmen molekul PLA menjadi mudah untuk menghasilkan peningkatan X_c. Berdasarkan persamaan Hoffman-Weeks, nilai suhu kesetimbangan (T_m°) untuk PLA tulen dicatatkan pada 201.08 °C. Kadar pertumbuhan spherulit PLA tulen dan PLA/CSIM campuran diukur dan dianalisis dalam julat suhu 95 hingga 125 °C oleh mikroskop polarisasi optik (POM). Kadar pertumbuhan spherulit PLA dipengaruhi oleh T_c dan kandungan CSIM dalam campuran PLA/CSIM. Apabila T_c meningkat (100 °C$\leq T_c \leq$ 110 °C), saiz spherulit meningkat dan pembentukan kepadatan nukleus menjadi lebih padat. Di dalam julat T_c tersebut, jelas bahawa spherulit telah mengalami pelanggaran lengkap dalam masa 5 minit untuk kandungan CSIM yang rendah seperti PLA/CSIM1 dan PLA/CSIM3 campuran. Walau bagaimanapun, peningkatan dalam suhu penghabluran ($T_c \geq 115$ °C) telah menurunkan pembentukan ketumpatan

nukleus manakala saiz spherulit meningkat. Pada T_c yang sama, kandungan CSIM yang semakin meningkat hampir tidak menjejaskan saiz spherulit. Berdasarkan teori Hoffman-Lauritzen, nilai tenaga diperlukan untuk pembentukan saiz kritikal nukleus (K_g) PLA adalah 6.69 x 10^5 K^2 dan rejim III telah digunakan untuk menyesuaikan data eksperimen.

THE EFFECTS OF CORE SHELL IMPACT MODIFIER ON PROPERTIES AND CRYSTALLIZATION BEHAVIOUR OF POLY(LACTIC) ACID

ABSTRACT

Polylactic acid (PLA) was melt-blended with different contents (0 to 30 wt%) of a commercially available core shell impact modifier (CSIM). Neat PLA and PLA/CSIM blends were prepared via an internal mixer and compression molded into test specimens. Thermal, mechanical and morphological properties of neat PLA and PLA/CSIM blends were studied. The neat CSIM showed shell, interphase, and core regions when observed under transmission electron microscopy (TEM). Each region in the neat CSIM presented different glass transition temperature. The Fourier transform infrared spectroscopy (FTIR) confirmed that the shell and core of the neat CSIM was made of polymethyl methacrylate (PMMA) and polybutyl acrylate (PBA), respectively. An increased in CSIM content slightly decreased the ability of PLA to crystallize and/or re-crystallize, and the cold crystallization temperature shifted to higher temperatures. The matrix PLA showed good compatibility with the PMMA shell of CSIM. This was confirmed by the dynamic mechanical analysis (DMA) tests. In the thermogravimetric analysis (TGA), both of the neat PLA and CSIM displayed single step decomposition. Upon addition of CSIM, the stress-strain curves presented that the brittleness of neat PLA increased without the improvement in ductility. Tensile stress, tensile modulus, and elongation at break of PLA decreased; yet, the notched and un-notched impact strength increased as CSIM content increased. Scanning electron microscopy (SEM) micrographs revealed that with the addition of CSIM contents of 5 to 30 wt%, the fractured surface became rougher than neat PLA. Voids were observed which likely caused by the pull-out of CSIM during

fracture. The clarity of the PLA was tested using chromameter. Incorporation of CSIM did not affect the clarity of the PLA except at 30 wt% contents of CSIM. The isothermal crystallization kinetics of neat PLA and PLA/CSIM blends were studied by differential scanning calorimetric (DSC) and data obtained were analyzed with the Avrami equation. The results showed that the crystallization rate is controlled by the crystallization temperature and the incorporation of CSIM content. The maximum crystallization rate, $\tau_{1/2}$ was observed when PLA was blended with 1 wt% CSIM and isothermally crystallized at 105 °C. The result trend for degree of crystallinity (X_c) are comparable to the crystallization rate ($\tau_{1/2}$) versus crystallization temperature (T_c). The increased in higher $T_c \geq 110$ °C has made the mobility of PLA molecular segment become easy to facilitate resulting in the increase of X_c. Based on the Hoffman-Weeks equation, the equilibrium temperature (T_m°) value for neat PLA was recorded at 201.08 °C. The spherulitic growth rate of neat PLA and PLA/CSIM blends was measured and analyzed in the temperature range of 95 to 125 °C by polarized optical microscopy (POM). The spherulitic growth rate of PLA was influenced apparently by the T_c and the CSIM content in the PLA/CSIM blends. As the T_c increased (100 °C $\leq T_c \leq$ 110 °C), the spherulites size increased and the formation of nuclei density became denser. At this T_c range, it is apparent that the spherulites have undergone complete impingement within 5 minutes for low CSIM contents such as PLA/CSIM1 and PLA/CSIM3 blends. However, further increased in crystallization temperature ($T_c \geq 115$ °C) has lowered the formation of nuclei density while spherulites size increased. At the same T_c, the increased in CSIM contents almost did not affect the spherulites size Based on the Hoffman-Lauritzen theory, the energy require for the formation of nuclei's critical size (K_g) value of PLA was 6.69 x 10^5 K^2 and regime III was applied to fit the experimental data.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Plastics have been the most used material in the world, playing central role in modern industrial economies. However, the growing reliance on petroleum-based polymers such as polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET) (Balakrishnan et al., 2010) has raised several environmental issues (Molinaro et al., 2013). For example, the persistence of petroleum-based polymers in the environment which is not readily biodegradable and resistance to microbial degradation has led towards the scarcity of landfill space (Avérous and Pollet, 2012, Abdelwahab et al., 2012). Moreover, the decrement of petroleum resources and the concerns over emissions of toxic gases during incineration have driven efforts to develop biodegradable polymers from renewable resources (Abdelwahab et al., 2012).

Biodegradable polymers are expected to be an alternatives for petroleum-based plastics due to the limited sources and increased in petroleum price which will restrict their usage in the near future (Balakrishnan et al., 2010). Biodegradable polymers are also can be degraded through the action of enzymes or chemical deterioration associated with living organisms (Vroman and Tighzert, 2009). There are several biodegradable polymers that has been developed. Aliphatic polyesters is a part of the biodegradable polymer groups which consists of polylactic acid (PLA), polyglycolic acid (PGA), polycaprolactone (PCL), and polyhydroxybutyrate (PHB). However, PLA which is a linear aliphatic biodegradable polyester derived from

biomass through bioconversion and polymerization has become a potential candidate for various large-scale industrial applications (Kumar et al., 2010).

PLA has several advantages such as renewable resources, biodegradation, biocompatibility, excellent thermal and mechanical properties, and superior transparency of the processed materials (Wu and Wu, 2006). The production cost is high during the early development of PLA. Hence, it has been primarily used only for medical applications such as internal sutures, implant devices, and tissue scaffolds (Molinaro et al., 2013) due to its high biocompatibility and biodegradability in the human body (Murariu et al., 2007). Nowadays, PLA must possess good mechanical properties and stabilities to prevent degradation and maintain high molecular weight to be processed in a mass scale into packing, textile and general plastic materials (Zhang and Wang, 2008). Unfortunately, PLA shortcomings such as brittleness, and lower impact resistance at room temperature which results in splitting and other handling problems during sheet manufacturing (Afrifah and Matuana, 2010); are preventing its large scale competition with petroleum-based polymers (Fowlks and Narayan, 2010).

Several modifications such as plasticization, copolymerization, and blending of PLA with biodegradable and non-biodegradable polymers have been suggested to enhance the mechanical properties of the neat PLA (Kumar et al., 2010). The toughening of PLA by blending with rubber will result in an expensive blend. However, blending the PLA with inexpensive non-biodegradable polymers such as polyethylene and polyisoprene will require compatibilizers to improve the miscibility between the polymers (Kumar et al., 2010). Addition of suitable impact modifier will improve the toughness of PLA. Arkema has introduced core shell impact modifier

under the trade name Biostrength 282. These core shell impact modifier (CSIM) are designed to improve the toughness of the PLA and to maintain the clarity of the PLA.

1.2 Problem statements

PLA are readily toughened by blending with rubber provided that an appropriate rubber particle is incorporated during mixing and there is adequate adhesion between PLA and rubber phases (Jaratrotkamjorn et al., 2012, Bitinis et al., 2011). There are some factors influence the adhesion such as physical interactions or chemical reactions between the two phases which also generally have a strong effect on blend morphology. Hence, it is usually impossible to vary interphase adhesion and particle size in a totally independent way (Lu et al., 1996). Moreover, the absolute and relative rheological characteristics of the matrix and rubber phases are important factors during mixing that determines the final rubber particle size in the blends (Lu et al., 1996).

Instead of using a rubber that has to be broken up during blending process, it is also possible to work with pre-shaped particles. These materials are supplied as watery emulsions or as precipitated agglomerates. To prevent the rubbery particles stick together, they are given a hard shell. In the blending process, these core shell impact modifiers (CSIM) have only to be deagglomerated (Gaymans and Werff, 1994). Good physical interaction, or even miscibility of the chains forming the shell with those of the matrix often permit this ideal to be achieved (Lu et al., 1996). The CSIM are frequently used in the toughening of polyesters (Gaymans and Werff, 1994).

The study related to the crystallization phenomena is vital in polymer processing, for several reasons. For example, in the final stage of the polymer processing, the control of the temperature profile during cooling determines the development of a specific morphology which influences the final properties material (Iannace and Nicolais, 1997). However, the crystallization rate of the PLA is extremely low in comparison with other commercial thermoplastics despite of having many desirable properties. The high degree of crystallinity in PLA is difficult to achieve. In this case, the amorphous content of PLA plays a very important role on the final properties of the articles. The presences of additives in a neat polymer resin can influence the crystalline morphology and kinetics. The additives can either provide nucleating sites for initiating the crystallization or increase the polymer chain mobility and thus enhancing the crystallization rate (As'habi et al., 2013).

The study of crystallization behaviour of polymers can be carried out either in isothermal or non-isothermal crystallization kinetics. This study is focus on isothermal crystallization kinetics of PLA. An understanding of the kinetic of the crystallization process is important for the selection of processing parameters such as mold temperature and hold time during injection molding. Isothermal crystallization is a popular method to obtain kinetics data by rapidly cooling the sample from the melt to the crystallization temperature and measuring the heat evolved while the sample is held isothermal (Foreman and Blaine, 1995). To the best knowledge, no work study has been reported on the isothermal crystallization behaviour of the PLA/CSIM blends system. This was achieved through calorimetric analyses and examination of the spherulitic evolution through polarized optical microscopy (POM).

1.3 Research objectives

The present study investigates the effect of incorporation core shell impact modifier in PLA matrix system. Mechanical, thermal and crystallization of the PLA/CSIM blends were studied. The objectives of the present study are as follows:

1. To characterize the core shell impact modifier.

2. To study the effect of the core shell impact modifier at different contents on the thermal and mechanical properties of PLA and PLA/CSIM blends.

3. To investigate the effect of different isothermal crystallization temperature and CSIM contents on the crystallization behaviours of neat PLA and PLA/CSIM blends.

1.4 Scope of research

The present study focuses on the fabrication of the neat PLA and PLA/CSIM blends. The first phase study highlights on characterization, thermal, and mechanical properties of the neat PLA and PLA/CSIM blends by using TGA, DSC, DMA, tensile and impact testing machine. The second phase concentrates on the study of the isothermal crystallization kinetics of the neat PLA and PLA/CSIM blends at different CSIM contents and various crystallization temperatures by using DSC. The third phase emphasizes on the crystal growth of the neat PLA and PLA/CSIM blends. This study was carried out by using POM.

1.5 Dissertation overview

Chapter 1 starts with the introduction of the project. It covers brief introduction about research background, problem statements, research objectives, scope of researches and dissertation overview.

Chapter 2 contains the literature review on several related topics which includes PLA, CSIM, and crystallization behaviour.

Chapter 3 describes materials specifications, equipment used, and experimental procedures that have been carried out in this research such as tensile test and DSC for the isothermal crystallization kinetics study.

Chapter 4 reports the characterization of raw materials used in the blending preparations. It is divided into three parts. The first part describes the characterization of raw materials and blends. The second part discusses the isothermal crystallization kinetics of PLA and PLA/CSIM blends. The last part explains the crystal growth of the PLA and PLA/CSIM blends.

Chapter 5 concludes the findings from this research and also some recommendations for future works in this related field.